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The Examination of Crude Synthetic Gasoline for the Purpose of (A) Obtaining Isoprene and (B) Reducing the Amount of Unsaturated Hydrocarbons

THE EXAMINATION OF CRUDE SYNTHETIC GASOLINE FOR THE PURPOSE OF (A) OBTAINING ISOPRENE AND (B) REDUCING THE AMOUNT OF UNSATURATED HYDROCARBONS

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

ARTHUR WELLESLEY HAYFORD

ENTITLED THE EXAMINATION OF CRUDE SYNTHETIC GASOLINE FOR THE PURPOSE OF (A) OBTAINING ISOPRENE AND (B) REDUCING THE AMOUNT OF UNSATURATED HYDROCARBONS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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I INTRODUCTION

The development of distillation of petroleum oils under pressure to meet the increased demand for motor fuel has resulted in the production of a large quantity of "crude, synthetic gasoline". The commercial name "untreated pressure still distillate" suggests the source of this kind of gasoline. In this paper, a light, untreated distillate produced by the effect of heat and pressure upon a heavier petroleum product is regarded as a crude, synthetic gasoline.

The process of development of pressure distillation of petroleum oils has always presented many interesting problems. Some have been satisfactorily solved, but others are still open to investigation and are being diligently studied. One of the latter deals with the unsaturated content of crude distillate from the cracking stills. In 1919, an average of 10,100,000 barrels of crude oil was produced per month. Of this amount, about 8% was lost in the sulphuric acid refinement. Therefore, any investigations is justified that has as its object the reduction of this loss or the possible utilization of a part of these unsaturated compounds. The presence of isoprene in sufficient quantity in cracked light oil fractions to warrant its separation and preparation for use in the synthesizing of rubber was elected as one possible means of offsetting this loss incurred by sulphuric acid treatment. The prevention of the formation of these unsaturated hydrocarbons in the pressure stills, either by hydrogenation or by a special adjustment of distillation conditions, is another

method of attaining the same purpose.

The experimental work was divided among four subjects: Part I (A) Isoprene from Petroleum Products (B) Isoprene from Turpentine Part II (A) Hydrogenation of Gasoline (B) Recombination of "Permanent" Gases with Gasoline. Any one of these four divisions is a problem worthy of an investigation that would requir more time than was allotted the entire research. The primary object, however, was a broad examination of the unsaturated content of pressure still gasoline and its future possiblities.

The gasoline used in the experimental work was kindly supplied by the Standard Oil Company (Indiana). It is the lightest fraction (specific gravity) condensing from a Burton Pressure Still

II HISTORICAL

Part I

(A) Isoprene from Petroleum Products

A paper written by Dr. Ossian Aschan[1] describing his work on the pyrogenic decomposition of Russian "masut", stating that isoprene can be readily and practically obtained from Russian Oils by a cracking process, prompted this part of the investigation. Though Russian oils and mid-continental crude oils are basically different, the changes occurring in a pressure still are very complex and it is impossible to predict the resulting products. For that reason, Dr. Aschan's theory that isoprene obtained from Russian oils is the result of the reduction of cyclic compound, which is not present to any extent in mid-continent crude oil, should not divert an examination of this gasoline. If isoprene is formed from mid-continental oils by the severe action of heat and pressure, it will probably be found in the first fraction condensed from the pressure stills.

The "masut" decomposed by Aschan is that portion of the crude petroleum that remains after the kerosene and naphtha fractions have been removed. It corresponds in this respect to the oil that is charged in pressure stills in the mid-continent refineries. Aschan fractionated the lightest condensate resulting from the pyrogenic decomposition of "masut" and to the portion boiling between 32-35° C applied a few qualitative tests. A positive proof of the presence of isoprene or a hydrocarbon containing the necessary conjugated linkage was obtained. No previous chemical

separation was required.

The writer did not succeed in finding any reports in the journals relative to the recovery of isoprene from American Petroleum. California oil has been examined and isoprene has been obtained from it. Mr. A. H. King[2] in his review of the synthetic rubber situation, states that petroleum oils will be the probable source of isoprene in the future. The increased activities to perfect the synthesis of rubber encourages further research in this field.

(B) Isoprene from Turpentine

A number of syntheses of isoprene have been tried and many patented. Three principal processes that met with varying degrees of success and which are being investigated at the present time are: (1) preparation by the destructive distillation of certain petroleum residues (2) dehydration of secondary and tertiary alcohols and (3) the heat decomposition of pine oils or turpentine.

Tilden[3] is credited with the first preparation of isoprene by the destructive distillation of turpentine. He used an iron tube 1-2 meters in length and heated it to dull redness for cracking of turpentine vapors. The material used was commercial American turpentine. The vapors escaping from this tube were liquified in a long condenser cooled by a freezing mixture. By returning oil that boiled above 140° C for further heat treatment he was able to obtain a yield of 6.25% of hydrocarbons that boiled between 33-40° C. By very careful and repeated fractionation Tilden separated the 33-35° C fraction which upon combustion gave the empirical

formula C_5H_8.

Harries and Gottlieb,[4] using an isoprene lamp, succeeded in obtaining isoprene in amounts varying with the composition of the turpentine oil used. They concluded from the results of their experiments that limonene, a dipentene boiling at 177° C, would yield uponproper heat decomposition 30-50% of isoprene. Pinene, however, boiling at 156° C, yielded only a small amount of isoprene about 1%, upon similar treatment.

Two American chemists[5] tried experiments with the isoprene lamp upon American turpentines. They treated different fractions separately, one known to be mostly limonene, the other mostly pinene. Their results showed 5.5% isoprene from the 177° C fraction and 8% isoprene from the 156° C fraction.

Thus it can be seen that the literature and data upon this subject is rather contradictory and confusing and it is still undecided as to the source that will produce the greater amount of isoprene by heat composition. It is not the object of the experiments performed on the destructive distillation of turpentine to determine the respective yields of isoprene from pinene and limonene, but rather to produce a substance known to be high in isoprene so that it will be possible to study its physical and chemical properties.

Part II

(A) Hydrogenation of Crude Synthetic Gasoline

The simplest method of reducing unsaturation in pressure still gasoline, thereby lowering the cost of refining, is to pre-

vent the formation of the undesirable compounds in the still. Many special processes have been patented that tend to accomplish this desired saturating of the distillate. Some of the more prominent types may be classified as follows:[6] (1) Direct hydrogenation of the mineral oil vapors in the presence of finely divided platinum or palladium (2) Passing a mixture of oil vapors and steam over hot iron, alumina, nickel rods, carbon, etc. (3) Passing oil vapors over finely divided nickel (4) Distilling oil over $AlCl_3$ at atmospheric pressure (5) Condensation under pressure.

None of the first three classes are being operated in this country on a large scale. The fourth method has been supported and extensively examined by the Gulf Refining Company. The principal objection to this process is the additional expense and labor necessary to recover the $AlCl_3$.

The fifth, commonly known as the Burton Process, is by far the most important, producing a large part of the "synthetic" gasoline in this country. The enormous distillation and cheapness of operation of the Burton Still has done much to discourage the development of the above named processes. The gasoline used inthese experiments came from a Burton pressure still.

(B) Recombination of "Permanent" Gases

The term "permanent" gases means those gases that are mechanically held in solution in the pressure distillate and that are liberated upon distillation at atmospheric pressure and not condensed by ordinary methods. The boiling points of these gases

are below 0° C.

The method of reducing the unsaturation is not particularly a new field, but it is one that is in the process of commercial development. Consequently, what publications there are, are mostly patent descriptions. The McAfee process,[7] referred to above as the $AlCl_3$ process, is consistent with some of the principles applied in this part of the research.

Another application is illustrated by the practice of a large mid-continental refinery of pumping their pressure stills up to 95 pounds per square inch, with the gases from a previous distillation, thereby reducing to some extent the formation of more gases.

III EXPERIMENTAL

Part I

(A) Isoprene From Petroleum Products

1. Preliminary discussion

It would be well to briefly review some of the properties of isoprene.

Isoprene is a hemiterpene, the lowest member of the terpene series. It has the property of polymerizing under the action of certain condensing reagents such as concentrated hydrochloric acid, metallic sodium or exposure to heat and light, to form a caoutchouc like substance. Other compounds, especially piperylene (1-3 Pentadiene B. P. 42°), 3 Me-2-4 pentadiene B. P. 76°, cyclo pentadiene B. P. 41° and butadiene B. P. 1°, have been successfully polymerized. These "dienes" are all characterized by the fact that they contain a conjugated linkage

$$C = C - C = C$$

The paper mentioned previously on isoprene from "masut" was used as a guide in this part of the experimental work. The fraction containing isoprene was subjected to the polymerizing action of $AlCl_3$ and sodium, and the addition of hypochlorous acid ($HClO$) resulted in a compound resembling in every way isoprene dichlorhydrin, $C_5H_8(ClOH)_2$. He was, therefore, justified to conclude that isoprene was one of the products of the destructive distillation of "masut". The gasoline examined was not subjected to any further heat treatment. Careful fractionation and testing

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

the proper fraction in the manner advised by Ashan was the general method of procedure.

2. Method of procedure

(a) General data

Physical and chemical properties of the crude gasoline used in these experiments were:

Color - water-white

Odor - disagreeable, slight resemblance of terpenes

Specific Gravity - .698-.707 (increases upon exposure to the atmosphere)

Distillation Record No. 1

		"Gas Free"		"Original"
Initial B. P.		38°		23°
Percent		Temp. °C		Temp. °C
0 - 10		38 - 78		23 - 67
10 - 20		78 - 84		67 - 77
20 - 30		84 - 89		77 - 85
30 - 40		89 - 93		85 - 92
40 - 50		93 - 97		92 - 97
50 - 60		97 - 101		97 - 102
60 - 70		101 - 105		102 - 107
70 - 80		105 - 112		107 - 114
80 - 90		112 - 121		114 - 134
90 -	97.5%	121 - 154	91.5%	134 - 146
		2% Residue		1% Residue
		.5% gas by difference		7.5% gas by differ.

	"Gas Free"	"Original"
Sulphuric Acid Absorption (89%)	21.3 - 23%	27 - 29.5%
" (7% excess SO_3)		38.8%

(b) Fractionation of the Gasoline

Five hundred twenty-six grams (750 cc.) of gasoline were distilled. A special form of distilling column 10 inches long and containing seven wire screens of 100 mesh, separated by glass cylinders a little smaller in diameter than the column, was used. This arrangement caused a thorough washing of the condensed vapors and gases.

First fraction:		
23° - 75°	165 grams	31.4%
Second fraction:		
23° - 41°	23.52 grams	4.5%

If a colder condensing system had been employed a larger yield of this fraction could easily have been obtained.

(c) Qualitative tests

Twenty-five cubic centimeters of this fraction were slowly distilled over metallic sodium. A short fractionating column of the same pattern as described above was used. The portion boiling between 30-40° C was saved and refractionated over fresh sodium. About 13 grams were obtained in this manner and this oil was considered the portion that would obtain isoprene if any was present. Though Aschan tested a narrower fraction, 33=35° C, the boiling point of isoprene is given by several authorities as 37-38° C, accounting for the larger range used in this case.

Five cubic centimeters of this liquid were sealed in a glass tube with 1 gram of freshly cut metallic sodium. This tube was suspended over a steam jet. Another sample of 3 cc. were added to a tube containing 0.1 gram of $AlCl_3$ (anhydrous). This tube was also tightly stoppered and exposed to a temperature of 100° C. No immedaite change took place in either case. After a period of 24 hours the liquid in the $AlCl_3$ tube became yellowish and turbid. The tests were not observed again until 10 days after, at which time it was noticed that a dirty yellow color was imparted to each oil, but there was no apparent change in viscosity of the oils even on cooling. Inasmuch as these tests furnished no positive evidence of iosprene, or similar compounds that polymerize with these reagents, the hypochlorous reaction was not performed.

(B) The Preparation of Isoprene by the Destructive Distillation of Turpentine

1. Preliminary Discussion

This investigation was carried out in connection with the preceding work. It was originally intended to devote the entire time to the recovery of isoprene from synthetic gasoline and in order to become familiar with the compound and its properties, turpentine was destructively distilled for the purpose of obtaining isoprene

2. Method of Procedure

The process of destructive distillation was fundamentally the same in all of the following experiments. Turpentine oil was

dropped from a separatory funnel upon some hot pieces of porcelain plate in the bottom of a distilling flask. The turpentine was immediately vaporized, and in most cases the vapors were slightly superheated before leaving the flask. The thermometer at the outlet tube showed an increase from 3-9° C above the normal boiling point of the oil used. The vapors then passed through the cracking tube. This tube was a hard glass tube, supported and insulated by magnesia pipe covering. The source of heat was supplied by an internal coil 30 inches in length of No. 18 Nichrome wire wound from 35 feet of the wire. The temperature could be maintained fairly constant within 10° by adjusting a carbon plate rheostat which was connected in series. The temperature was measured by a base metal thermocouple and a Hoskins pyrometer.

The cracked vapors were then led to an 18 inch spiral condenser. At first the temperature of the circulating water was kept between 50 and 55° C in the attempt to fractionally condense the vapor. The lower boiling products such as isoprene would pass on to a second receiver which was immersed in a salt and ice mixture. The system of fractional condensation was later abandoned and the circulating water and two receivers were maintained at as low a temperature as possible. The combined condensates were later fractionated.

The temperature and rate of distillation were varied for the purpose of determining thebest condition to produce a maximum yield of low boiling hydrocarbons. For results see Table I.

TABLE I

Heat Decomposition Of Turpentine

Run Number	3	4	5	6	7	*8	3a	6a	6b
Vol. Oil Distilled, cc.	460	400	80	81	180	200	121	110	173
Vol. Oil Condensed, cc.	426	370	67	71	170	187	109	92	162
% by Volume Condensed	92.5	92.4	83.5	87.5	94.5	93.5	90.0	83.5	93.5
Oil Bath Temperature, °C	185	185	190	190	195	185	210	185	
Av. Temp. Vapors in Distilling Flask, ° C	158	159	161	162	165	160	142 145	156	168 172
Rate of Distillation cc. per hour	110 120	120	20	75 90		75			
Temp. Cracking Tube, °C	500	400	550 600	350	350	500	600	500	500
Yield Below 55°C, % by vol.	6.5	6.25	5.0	7.4	7.8	none	3.3	2.0	2.0
Carbon Deposit (slight, medium, heavy)	M	S	H	S	S	none	H	H	H
Formation of Vapors (slight, medium, heavy)	M	S	H	S	S	M	H	H	H
Color of Condensate	red	straw yellow	deep red	straw yellow	pale yellow	orange	dark red	dark red	dark red

* Cracking tube filled with pieces of broken pumice

3. Remarks on Experiment

Material Distilled:

Runs Nos. 3, 4, 5, 6, 7 and 8 - Commercial American Turpentine (98% between 154 and 157°C)

Run No. 3a - The 56-156° Fraction from Run No. 3

Run No. 6a - The 56-160° Fraction from Runs No. 4, 5 and 6

Run No. 6b - The 160-177° Fraction From Runs No. 4, 5 and 6

The first cut at 55° C was chosen because there was a distinct pause at that temperature. In most instances, the distillation stopped entirely at 42° C, but in all cases there was a distinct lapse at least at 55° C.

The condensate of Run No. 3 showed the following distillation record:

Distillation Record No. 2

Percent	Temperature
0 - 10	29 - 120°
10 - 20	12 - 143°
20 - 30	143 - 154
30 - 40	154 - 159
40 - 50	159 - 163
50 - 60	163 - 170
60 - 70	170 - 179
70 - 80	179 - 192
80 - 90	192 - 210
90 - 98	over - 210

2% Loss

The combined condensate was then fractionated into four parts:

First	29.5 - 55°	30 cc	= 6.5%	"Isoprene"
Second	55 - 157°	121 cc	= 26.4%	"Pinene"
Third	157 - 177°	139 cc	= 30.2%	"Limonene"
Fourth	177 - above	130 cc	= 28.3%	"Residue"

Attempts to decompose the higher fractions were unsuccessful due to excessive formation of carbon, causing the cracking tube to become clogged.

4. Qualitative Reactions on the "Isoprene" Fraction

A 25 cc. sample of the 30-55° fraction was distilled over metallic sodium. A short column containing six wire mesh supported by glass cylinders served to effect a more efficient separation. Most of the oil distilled between 31.5° and 40° C.

Ten cc. of the above fraction were added to a glass tube that contained a small amount of anhydrous $alcl_3$. The tube was sealed and placed in a beaker of hot water. 10 cc. more of the sample were added to another tube that contained 1 gram of freshly cut sodium. Both tubes were warmed in the same beaker. After 48 hours, a decided change in color and viscosity was apparent. These tests were not again observed until two weeks later, at which time it was noticed that both oils had changed from a very fluid colorless liquid to a viscid opaque yellow substance. These results compare favorably with those described by Aschan in his work upon isoprene.

These experiments were not continued after a sufficient

quantity of low boiling products was obtained to satisfactorily test the qualitative reactions of isoprene.

Part II

(A) Attempts to Decrease the Unsaturated Constituents in Crude Synthetic Gasoline by Hydrogenation

1. Preliminary Discussion

When a petroleum oil is distilled, especially under pressure, cracking invariably occurs. The heavy hydrocarbons are the first to break down and usually the lighter ones follow as the temperature is raised. The resulting products vary from hydrogen to carbon. One law, however, is observed. When a paraffine molecule breaks down into two molecules, one of them must contain an insufficiency of hydrogen, that is, one molecule is unsaturated.[8] Frequently, the products are not so simple, many other changes taking place and prolonged exposure to high temperatures will produce hydrogen, methane, ethylene and other permanent gases. Substances high in carbon will also be formed. The lighter liquid hydrocarbons that are condensed will consist of paraffines together with naphthenes, olefines and aromatics.

In order to effect any reaction certain conditions must be met to permit any reaction at all, and secondly, there is a definite range of conditions within which any desired reaction is accomplished most efficiently. It is the opinion of the people interested in this problem that reduction of unsaturation is a time, temperature and concentration reaction. Just as the cracking of a hydrocarbon molecule is effected by exposure of the molecule to a certain temperature for a certain period of time and

the subsequent removal from the reaction zone of one or more of the decomposition products, resaturation, as it may be called, is possible and can be achieved if the proper temperature, the right period of exposure and the correct components are present in their right proportion in the zone of reaction. That is not imposing too many limitations as one condition,namely, duration of exposure can be reduced to a minimum if that particular temperature can be determined at which the desired reaction is carried out in a period of time that approaches zero.

The progress from left to right of the reaction $C_nH_{2n} + H_2 = C_nH_{2n+2}$, is dependent upon at least two conditions, temperature and proportion of hydrogen to olefine. Other conditions will have an influence upon the speed of the reaction such as removal of the products and the introduction of a suitable catalyst to aid interation. Applying again the foregoing reasoning, there is fundamentally a particular narrow range of temperature and one specific ratio of concentrations of the interacting substances necessary for this reaction. The determination of the specific set of conditions for a certain reaction is a matter of trial. To attempt to establish the proper conditons under which the reduction of the unsaturated hydrocarbons in the pressure stills may be accomplished is entirely too comprehensive and difficult to be handled at this time.

A few experiments were performed keeping this object in view, with the expectation that some of the results would indicate a profitable method of attack.

2. Sulphuric Acid Absorption[9]

The method of ascertaining the amount of olefines in the gasoline, though chosen arbitrarily, served sufficiently well to furnish a basis of comparison. Eighty-nine percent H_2SO_4 was t taken as the best strength of acid to absorb the olefines probably present in the gasoline. This strength of acid was used to absorb the olefines in a kerosene oil in the work performed by Dr. E. E. Charlton.

A 2 cc. pipette was calibrated to deliver the required volume into a Babcock bottle. The oil was run in first and cooled in an ice bath. Eighty-nine percent sulphuric acid was added, 10 cc. at a time, shaking between each portion. Enough acid was added to bring the upper meniscus of the oil to the 90% mark. The bottle was then centrifuged for 10 minutes. Further centrifuging does not cause any more separation. The volume of clear oil is read and that reading subtracted from 100 will give the percent of olefines absorbed. The compounds absorbed may not be altogether olefines, as other hydrocarbons, cyclic or aromatic, may be partially effected by 89% sulphuric acid.

If the tests are carried out under the same conditions, this method serves as a ready basis of comparison for the degree of unsaturation.

Sulphuric Acid Absorption

Test No.	Original Sample	Degasified Sample	Treated Sample
1	27.0%	21.1%	
2	27.5	21.8	
3	27.8	20.9	
4	29.0	23.0	
19a		22.3	20.5%
21		22.3	20.3

3. Method of Procedure

(a) Hydrogenation by Heat

The first attempts to hydrogenate the gasoline was done by simply mixing hydrogen with the vaporized gasoline and leading the mixture through a long internally heated tube, condensing the oil vapors and determining the change in the sulphuric acid absorption of the oil.

A known quantity of gasoline was allowed to drip into a side neck U-tube which was immersed in a sulphuric acid bath. Hydrogen was led into the U-tube through one of the side necks and was there mixed with the gasoline vapors. The mixed vapors then passed through a 36 inch hard glass tube which contained 35 feet of No. 18 Nichrome wire wound into a spiral coil 30 inches long. This coil furnished the direct source of heat.

The resulting products were led through an 18 inch spiral condenser that was connected in turn to two receivers in series, immersed in a salt and ice mixture. In all of the experiments, no

condensate collected in the second receiver indicating that all of the easily condensable vapors had been previously removed. The remaining gases bubbled through a water seal which caused a small pressure of 12-15 cm. of water to be maintained in the system. For results see Table II.

An explanation of a few of the quantities in this table is necessary. In order to approximate the weight of the unsaturated products present, an average compound was determined by considering all of the probable unsaturated, aliphatic hydrocarbons that would be in the oil, having a boiling point lying between 30 and 146°C. This average compound would boil at 96° and is represented by heptene, an olefine that boils at that temperature. Its specific gravity is .703at 20° C. Thus, 200 cc. of gasoline which is 21.7% heptene by volume will contain 30.5 grams of heptene. Heptene whose molecular weight is 98.1 requires one molecule of hydrogen, molecular weight 2.01, to saturate it, therefore, $\frac{2.01}{98.1}$ x wt. of heptene, will give the required amount of hydrogen, provided that the assumptions are correct. At least four times the calculated amount was used in each case,assuring an excess of hydrogen.

(b) Treatment for the Removal of Sulphur [10]

The presence of sulphur compounds is known to have a poisonous action upon nickel. The gasoline used in these experiments was found to contain 0.118% of Sulphur, by the oxygen combustion method. A preliminary treatment of the gasoline to reduce the sulphur content was tried.

TABLE II

Hydrogenation Under Influence of Heat

Run Number	12	13	14	15
Vol. of Oil Distilled, cc.	200	195	150	150
Wt. of Oil Distilled, grams	141	138	106	106
Sulphuric Acid Absorption,%	21.7	21.7	21.7	21.7
Wt. of Unsaturated Oil, grams	30.5	29.8	22.9	22.9
Wt. of Hydrogen Required, grams	0.61	0.60	0.46	0.46
Wt. of Hydrogen Supplied, grams	2.5	2.5	4.8	4.1
Excess Hydrogen Ratio	4.1	4.2	10.4	9.0
Rate of Hydrogen Feed, cc. per hr.	9,330	14,000	29,400	26,100
Temperature of Oil, °C	500	500	320	330
Rate of Gasoline Feed, cc. per hr.	66	96	120	
Sulphuric Acid Absorption After Run,%	25.2	28.6	22.0	22.2
Carbon Deposit (slight, medium, heavy)	S	M	S	S

Material Used: "Degasified" Gasoline. Hydrogen from Universal Oxygen Co. Cylinder #271

The gasoline was agitated for five hours with one half of its volume of potassium polysulphide, made by dissolving sulphur in a strong solution of potassium sulphide. The sulphide layer was drawn off after agitation and the oil was washed twice with water, once with 20% NaOH and twice more with water, then dried over $CaCl_2$, filtered and finally distilled. Two determinations showed a reduction of sulphur to 0.089%.

(c) Hydrogenating in the Presence of a Catalyzer

The hydrogenating was carried out in a 500 cc. gas absorbing bottle. Two grams of nickel carbonate was suspended in 100 grams of neutral tallow oil and heated up to 275° C. At this temperature hydrogen was bubbled slowly through the tallow reducing the $NiCO_3$. Four hours was usually required to reduce the nickel carbonate completely to nickel. Gasoline was added by means of a separatory funnel. The vapors passed directly to a spiral reflux condenser. The condensed gasoline ran back into the still or hydrogenating chamber for further saturation. The hydrogen was collected in a large graduated bottle. The hydrogenating flask was heated by an electric furnace whose temperature could be controlled by a rheostat. At the end of a run the temperature was allowed to drop and the flask disconnected. The gasoline was then distilled out of the tallow with or without the aid of a stream of hydrogen gas. For results see Table III.

TABLE III

Action of Hydrogen upon Treated Gasoline in the Presence of Metallic Nickel

Run Number	19a	21	18
Volume of Oil Used, cc.	85	100	81
Temp. of Hydrogenating Flask, °C	150	125	100
Volume of Hydrogen Used, cc.	13500	19600	13500
Volume of Hydrogen Collected, cc.	7500	14000	13180
Sulphuric Acid Absorption Before Run, %	20.5	20.3	23.0
Sulphuric Acid Absorption After Run, % (Distilled with H_2)	20.2	18.0	
(Distilled without H_2)	17.6	16.6	29.3

Materials Used: Degasified-Desulphurized Gasoline
Hydrogen, commercial, from cylinder

(B) Recombination of Permanent Gases

1. Preliminary Discussion

One of the by-products of the pressure stills is the gas that is formed by the severe action of heat upon the more unstable hydrocarbons. The gases are mechanically forced into the distillate by the pressure maintained in the system. They gradually escape from this gasoline if exposed to the atmosphere. Upon redistillation, they are rapidly liberated and do not go into solution again with atmospheric condensation. The distillation record of an average sample of the original gasoline shows a loss of 7.5% by volume due to these gases that do not condense. The statement that a recombination of these gases is possible, provided that proper conditions are established, temperature, concentration, etc., is another application of the same principle used in Part II (A).

Owing to the lack of time, only two experiments were tried, one using metallic nickel, the other using NiO upon asbestos.

The "permanent" gases employed were obtained by literating the gases from the crude gasoline, the product being called "degasified" gasoline.

2. Method of Procedure

The same apparatus was used as in the hydrogenation in the presence of nickel experiments. The volume of "permanent" gases was measured before and after bubbling through the oil. The gases from Run No. 20 were analyzed. For results see Table VI.

TABLE IV

Recombination of "Permanent" Gases in the Presence of Ni and NiO

Run	17 (NiO)	20 (Ni)
Vol. Gasoline Used, cc.	100	50
Temp. of Flask, °C	150	140
Vol. Gas Used, cc.	12,560	6,520
Vol. Gas Recovered, cc.	11,700	5,330
Sulphuric Acid Absorption Before Run	23.0	23.0
Sulphuric Acid Absorption After Run	22.3	24.8

Analysis of Gas From Run No. 20

Carbon Dioxide	.5%
Air (excluded)	(24.0)
Olefines	51.6
Aromatics and Naphthenes	5.1
Hydrogen	2.3
Paraffines (diff)	40.5

3. "Degasifying" Gasoline

750 cc. of gasoline were heated in a one liter round bottom flask over a steam bath. The ensuing vapors traveled upward through a 24 inch Liebig condenser. The condensed gasoline dropped back into the flask. The escaping gases were led through a long flask maintained at a temperature of 0° C. From 6.5 to 30 grams of vapors condensed in this flask, the noncondensable portion passing on to a graduated receiver. An exposure to steam for three hours was sufficient to remove all of the gases held in solution. Heating to a higher temperature over a free flame did not liberate any more gases. Slow heating will tend to prevent the carrying over of condensable vapors. For results see Table V and for analyses see Table VI.

4. Bromination of Gases

A decrease of 6.2% in the sulphuric acid absorption occurs when the gasoline is freed from dissolved gases. This suggests that the gases are highly unsaturated. To verify this, the liberated gases from one run were led through a brominating train consisting of a $CaCl_2$ tube for drying the gases, two bromine bottles containing 5% bromine in CCl_4 and another $CaCl_2$ tube and a reservoir to collect the remaining gases. 4,450 cc. of gases were reduced to 1,515 cc.upon passage through this train and upon repassing through the bromine were further decreased to 1350 cc. This means approximately 69% of hydrocarbons absorbed by volume which is not consistent with the results of the analyses of the gases. The bromine solution probably reacted with considerably more than than the olefines.

TABLE V

"Degasifying" Pressure Distillate

Run No.	1	2	3	4
Gasoline Used, cc.	750	750	750	750
Sp.Gr. Original Gasoline at 20°C	.705	.707	.706	.694
Vol. Gases Liberated	11,135	10,800	11,325	10,670
Wt. of Condensate in Ice Trap, grams	12.5	30.0	20.0	6.5
Wt. of Degasified Gasoline, grams	505	496		
Wt. of Liberated Gases, grams	12.5	14		
Sp.Gr. Degasified Gasoline at 20°C			.729	.723

Note: A sample that had been opened to the atmosphere for about 3 months yielded 7,180 cc. of gas

TABLE VI

Analysis of Permanent Gases

Sample No.	18	20a	20b
Carbon Dioxide, CO_2, %	1.1	0.4	0.2
Air (O_2 x 5)	(7.5)	(16.5)	(18.0)
Olefines (conc.H_2SO_4)	44.9	44.0	43.6
Aromatics and Naphthenes	10.7	12.5	12.3
Carbon Monoxide	0.5		
Hydrogen	4.5	1.3	2.9
Paraffine Hydrocarbons	38.1	41.8 (diff)	41.0 (diff)

The bromides were washed and dried and fractionally distilled:

28 - 38°	-	about 5%		
93 - (?)°	-	about 2%	indicating	Ethylene Bromide
138 - 143°	-	about 70%	indicating	Propylene Bromide
Residue	-	about 23%	indicating	Higher Bromides

IV CONCLUSIONS

Part I

(A) Isoprene from Petroleum Products

Failure to obtain positive proof of the presence of isoprene in these experiments should not be accepted as conclusive evidence that isoprene is entirely absent. The only specific statement that can be made based upon these results is that in comparing these results with those obtained by Aschan, not enough isoprene is present in light, cracked gasoline to respond to the qualitative tests successfully applied to cracked Russian "masut". If any oil, more particularly one containing cyclic compounds, be subjected to pressure and heat, many transformations can be made to take place. Further cracking increases the quantity of light unsaturated hydrocarbons and the possibility of the formation of isoprene will likewise be increased.

California crude oil contains on an average of 40 % of cyclic hydrocarbons. These cyclic compounds can be opened and reduced under heat treatment to produce unsaturated, straight chained hydrocarbons giving California crude oil this advantage over mid-continental crude oil.

(B) Isoprene from Turpentine

It has not been the object of these experiments to devise an efficient method of producing isoprene by decomposing with heat. However, among the results obtained there is evidence, that if this type of distillation is to be used, the best operating con-

ditions observed so far are those of Run No. 7, employing a low cracking tube temperature and a slow rate of distillation. It was not possible to ascertain which terpene, pinene or limonene produced a greater yield of isoprene. The claim of Harries and Gottleib that isoprene may be obtained to the extent of 30-50% from a dipentene boiling at 176° C could not be verified due to the excessive carbonization in the cracking tube. It is apparently possible to obtain 5-8% of hydrocarbons boiling between 30-55°C by using this form of cracking apparatus and American turpentine which consists almost entirely of pinene.

Part II

(A) Hydrogenating Crude Synthetic Gasoline

An examination of the data of the hydrogenating experiments with heat along shows that the addition of hydrogen is not readily accomplished in this manner. An increase in the sulphuric acid absorption occurs in every instance. In this method of hydrogenation, the period of contact of hydrogen and oil vapors at the high temperatures is represented by the time of travel of the gases through the hot tube which is very fast. Application of pressure would lengthen the exposure of these gases to the desired temperature and also increase the concentration of hydrogen.

The period of exposure was increased in the second part of the hydrogenation experiments. Hydrogen could be bubbled through the oil for an indefinite length of time. In this case only a definite amount of oil can be used and when hydrogenation is complete the operation is stopped and the oil is separated from the

tallow by distillation. The introduction of a catalyzer suspended in the tallow oil evidently increases the addition of hydrogen. If the oil is distilled with the aid of hydrogen, the condensate will show a lower sulphuric acid absorption.

(B) Recombination of "permanent" Gases

Only two experiments were conducted in the attempt to effect a recombination of the "permanent" gases and the oil from which they came. These two experiments did not prove sufficient to permit the formulation of any conclusion. The particular problem offers an opportunity for the application of the hypothesis that a reaction of this type can be made to take place if the proper conditions are enforced upon the reacting molecules. The determination of these specific conditions involves the construction of a suitable form of reacting chamber or still, a convenient and reliable method of measuring the results of the experiments and the selection of a catalyzer to hasten the reaction.

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